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The use of symmetrized valence and relative motion coordinates for crystal potentials

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Symmetrized valence coordinates are linear combinations of conventional valence coordinates which display the symmetry of a set of atoms bound by the valence bonds. Relative motion coordinates are relative translations, or relative rotations, of two or more strongly bonded groups of atoms among which relatively weak forces act. They are useful for expressing interactions between molecules in molecular crystals and should be chosen, also, to reflect the symmetry of the interacting groups. Since coordinates defined by these procedures possess elements of symmetry in common with the bonding electron distributions, the force constants in the potential should be more amenable to calculation in terms of energy changes in the electronic ground state which accompany displacements of the atoms from equilibrium. It is easier to determine force constants for fitting experimental data because interaction constants coupling coordinates of unlike symmetry with regard to the crystal point group are necessarily zero. They may be small, also, for coordinates which belong to different representations of the local symmetry when this is not the same as for the crystal. Procedures are given for defining the coordinates, and for assuring that the potential energy is invariant to crystal translations and rotations. The secular equation is derived by expressing the kinetic and potential energies in terms of components of mass adjusted basis vectors which are chosen so that high and low frequency modes can be separated approximately. The necessity to remove redundancies among the coordinates in the potential is avoided.

I. INTRODUCTION

A. General ideas

This work is the outgrowth of efforts to express crystal potentials in terms of coordinates which are directly, or closely, related to the symmetry of the crystals. The idea was that the force constants would be more amenable to interpretation in terms of changes in the energies of the bonding electron distributions which accompany distortions associated with the excitations of the coordinates. It was desired, also, to achieve some practical advantages. Coordinates which behave differently under symmetry operations of the crystal cannot interact, and coordinates which behave differently under symmetry operations appropriate only to the atoms involved in the coordinates may still be small. Further, the equations expressing experimental data in terms of force constants are easier to apply in determining trial values. Finally, a diagonal force matrix will fit the data as well as a force matrix with diagonal and off diagonal elements using conventional coordinates.

Initially, the use of symmetrical combinations of valence coordinates was studied in applications to trigonal selenium. However, the idea emerged that the weak forces between the adjacent spiral chains might be expressed better by using relative rotations and relative translations of the atoms in primitive cells on adjacent spirals as coordinates. It was clear that such relative motion coordinates would be suited for expressing interactions between molecules in molecular crystals.

It is easy to define the relative motion coordinates so that translational invariance of the potential energy is achieved. However, rotational invariance requires either the use of properly defined linear combinations of some relative motion coordinates, or the introduction of properly selected interaction force constants between some of the coordinates. We experimented first by using rotationally invariant linear combinations of coordinates to make the trigonal selenium potential invariant. However, the procedure was rather cumbersome and the physical significances of some of the force constants was obscured. The idea of neglecting rotational invariance was then explored. It was possible to show that for a finite crystal the spurious terms which express couplings of the overall crystal rotations to the internal motions in the secular equation are negligible. However, the reviewer of an earlier manuscript on this subject pointed to other reasons why this procedure is not physically acceptable. In particular, the normal modes can be shown to be incorrect, and the force field which they imply must be wrong.

At this point methods for achieving rotational invariance by coupling selected noninvariant coordinates were studied. Quite simple procedures for doing this were developed and their application to trigonal selenium, as reported in the accompanying paper, met with success.

A method was also developed for obtaining the secular equation without the necessity of removing redundant potential coordinates while retaining the utility of having coordinates which permit approximate separation of high and low frequency modes. To do this the kinetic and potential energies are expressed in terms of components of mass adjusted basis vectors chosen so that some approximate displacement patterns are associated with

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high frequency normal modes and others low frequency normal modes. These coordinates can be normalized and made orthonormal and the secular equation is then diagonal in the part arising from the kinetic energy. It is not necessary to remove redundancies as long as the usual approximation which ignores any quadratic dependences of the potential energy coordinates on Cartesian displacements is used.[1]

B. Related work

There have been many adaptations of the Wilson FG method for molecules[2] to molecular crystals and to polymeric chains with regular repeat units. Higgs[3] gave an application to helical chains which is useful for biological polymers. Shimanouchi and co-workers have applied the FG method to crystals with special emphasis to the case of zero wave vector.[4] Their procedures are suited to calculating optically active vibrations and have been widely used, sometimes with adaptations.[5] Piseri and Zerbi have outlined a more general method suited to all wave vectors.[6]

In the FG method the kinetic energy is expressed using the same coordinates as are used to express the potential energy. These are chosen so that some coordinates take large force constants and others small. They are well suited to obtaining a secular equation that can be approximately factored into blocks giving high and low frequency normal modes, respectively. The disadvantages are that the kinetic energy matrix is not diagonal and redundancies must be removed if the potential energy coordinates are linearly dependent. In addition, the G matrix which arises from the kinetic energy is wave vector dependent. Further, if several coordinate models are being investigated in a search for the best force field a new G matrix must be obtained for each trial set.

Apparently the use of symmetrized valence coordinates has not been employed in crystal dynamics. A number of treatments of molecular crystals express the intermolecular potential in terms of translations and rotations of individual molecules.[7] This is an extension of the usual Born approach.[8] This procedure requires satisfying both translational and rotational invariance by proper selection of interaction force constants based on the symmetry operations of the crystal. The procedures to be described eliminate much of this work, and reduce the rest.

C. Special procedures

This work has led to significant computer automation which greatly speeded the final determination of the force field for trigonal selenium.[9] This work is limited to determining only a "basis" set of potential energy coordinates which are not transformed into each other by operations of the point group appropriate to the crystal (nonprimitive translation operations are included for nonsymmorphic crystals). All coordinates equivalent to these are determined by the computer. The force constants expressing interactions between coordinates in the basis set also apply to every set equivalent to this by symmetry. The computer program sets up force matrices which allow for the most general interactions. Finally, projection techniques are used to generate coordinates from an original mass adjusted basis set which serve to block diagonalize the secular equation according to the group of the wave vector.

II. SYMMETRIZED VALENCE COORDINATES

A. Coordinate definitions

Wilson *et al.*[2] have given procedures for calculating changes in bond distances, interbond angles, dihedral angles and all other valence coordinates likely to be of interest, in terms of the Cartesian displacements of the atoms bonded by the coordinates. The definitions insure that the coordinates are not excited by pure translations, or rotations, of the molecule containing the interacting atoms. The equation for the excitation H_i of a coordinate due to arbitrary displacements of the atoms in a molecule is

$$H_i = \mathbf{b}_i \Delta \mathbf{r} = \sum_\nu \mathbf{b}_{i\nu} \Delta \mathbf{r}_\nu \ . \tag{2.1}$$

where $\mathbf{b}_i$ is a row vector containing three elements for each atom in the molecule which operate on the components of that atom's displacement. All components in $\mathbf{b}_i$ are zero except those that pertain to the atoms whose displacements can excite the coordinate. These are the $\mathbf{b}_{i\nu}$ in the sum in Eq. (2.1), each $\mathbf{b}_{i\nu}$ being a row of three elements. The $\Delta\mathbf{r}$ and $\Delta\mathbf{r}_\nu$ in Eq. (2.1) are column vectors containing as elements the displacements of the atoms. Thus,

$$\Delta \mathbf{r} = \begin{bmatrix} \Delta \mathbf{r}_1 \\ \Delta \mathbf{r}_2 \\ \vdots \\ \Delta \mathbf{r}_\nu \\ \vdots \\ \Delta \mathbf{r}_n \end{bmatrix}, \quad \Delta \mathbf{r}_\nu = \begin{bmatrix} \Delta x_\nu \\ \Delta y_\nu \\ \Delta z_\nu \end{bmatrix} . \tag{2.2}$$

The first step in defining symmetrized valence coordinates for use in the crystal potential is to obtain a conventional set of coordinates which express the binding of a symmetrical group of atoms which are either in a single primitive cell, or in that cell and one or more neighbors. It is necessary that the coordinates belong to one, and only one, primitive cell.[10] The row vectors $\mathbf{b}_i$, which will be referred to as projection operators, are then determined by the Wilson procedures. Then each of the projectors is operated on by the operations of the symmetry group appropriate to the local symmetry to produce projection operators which define coordinates belonging to the irreducible representations of the local symmetry group. The usual methods of group theory are employed for this purpose.[11,12] This process is easily visualized because each $\mathbf{b}_i$ defines a displacement pattern of the atoms within the group and the group theory operations produce new vectors $\mathbf{b}_i$ which are linear combinations of the original set and define symmetrical displacement patterns.

The triangular X_2Y molecules of C_{2v} symmetry suffices to illustrate what this means. If the X atoms are numbered 1, 2 and the Y atom is number 3, the C_{2v} operations applied to the stretch $\Delta r(1,3)$ between atoms 1 and 3 gives two coordinates belonging to the A_1 and B_1 representations which are, respectively, symmetric and antisymmetric under the C_2 operations. They are

$$A_1:\ H_{sy,st} = \Delta r(1,3) + \Delta r(2,3) = [\mathbf{b}(1,3) + \mathbf{b}(2,3)]\,\Delta \mathbf{r}\ , \tag{2.3a}$$

$$B_1:\ H_{as,st} = \Delta r(1,3) - \Delta r(2,3) = [\mathbf{b}(1,3) - \mathbf{b}(2,3)]\,\Delta \mathbf{r}\ . \tag{2.3b}$$

It is readily seen that the operation C_2 moves the displacement pattern described by $\mathbf{b}(1,3)$ into the pattern for $\mathbf{b}(2,3)$. The operator for the X–Y–X angle bend goes into itself under all C_{2v} operations so this coordinate already has the group symmetry. The complete set is then

$$A_1:\ H_{sy,st} = \Delta r(1,3) + \Delta r(2,3) = [\mathbf{b}(1,3) + \mathbf{b}(2,3)]\,\Delta \mathbf{r}\ ,$$

$$B_1:\ H_{as,st} = \Delta r(1,3) - \Delta r(2,3) = [\mathbf{b}(1,3) - \mathbf{b}(2,3)]\,\Delta \mathbf{r}\ ,$$

$$A_1:\ H_{\phi} = \Delta\phi(1,3,2) = \mathbf{b}(1,3,2)\,\Delta \mathbf{r}\ . \tag{2.4}$$

If a triangular group of atoms with this symmetry is embedded in a crystal which possesses the C_2 operation there can be no interaction force constant between the coordinates of unlike symmetry. In more general cases there will be coordinates which belong to different representations of the local symmetry group, but belong to the same representation of the crystal group. Such coordinates can interact because the crystal symmetry prevails in determining which interactions are absolutely forbidden. However, even in these cases it may be reasonable to assume the interactions forbidden by local symmetry are small enough to neglect. This will happen if the electron distribution binding the interacting atoms conforms closely to the local symmetry.

In general the group of atoms for which the symmetrized coordinates are defined employ axes x, y, z which are inclined to the set X, Y, Z for the crystal. The projectors defined in terms of components along x, y, z must be converted to projectors valid for the X, Y, Z system. This is easily accomlished. Let i, j, and k be unit vectors along x, y, and z, respectively, and I, J, and K be unit vectors along X, Y, and Z. Then

$$[\mathbf{i}\ \mathbf{J}\ \mathbf{k}] = [\mathbf{I}\ \mathbf{J}\ \mathbf{K}]\,\mathbf{A}\ , \tag{2.5a}$$

$$\mathbf{A} = \begin{bmatrix} \mathbf{I}\cdot\mathbf{i} & \mathbf{I}\cdot\mathbf{j} & \mathbf{I}\cdot\mathbf{k} \\ \mathbf{J}\cdot\mathbf{i} & \mathbf{J}\cdot\mathbf{j} & \mathbf{J}\cdot\mathbf{k} \\ \mathbf{K}\cdot\mathbf{i} & \mathbf{K}\cdot\mathbf{j} & \mathbf{K}\cdot\mathbf{k} \end{bmatrix} \tag{2.5b}$$

and

$$\Delta \mathbf{r}_\nu = \mathbf{A}^T\,\Delta \mathbf{R}_\nu\ , \tag{2.6a}$$

$$\Delta \mathbf{r} = \{\mathbf{A}^T\}\,\Delta \mathbf{R}\ . \tag{2.6b}$$

In Eqs. (2.6a) and (2.6b), $\Delta\mathbf{R}_\nu$ is defined as in Eq. (2.2) with displacements ΔX_ν, ΔY_ν, and ΔZ_ν along X, Y, and Z being used. The $\{\mathbf{A}^T\}$ in Eq. (2.6b) denotes a matrix with $\mathbf{A}^T$ repeated n times down the diagonal, once for each atom in the group. Using Eq. (2.6b) the equation for a symmetrized coordinate H_i becomes

$$H_i = \mathbf{b}_i\,\Delta \mathbf{r} = \mathbf{b}_i\{\mathbf{A}^T\}\,\Delta \mathbf{R} = \mathbf{B}_i\,\Delta \mathbf{R}\ , \tag{2.7}$$

$$\mathbf{B}_i = \mathbf{b}_i\{\mathbf{A}^T\}\ . \tag{2.8}$$

If $\Delta\mathbf{R}_{cryst}$ denotes a column vector containing the $\Delta\mathbf{R}_\nu$ for all the atoms in all the primitive cells of the crystal the equation which calculates the excitation of a specific coordinate $H_i(l)$ belonging to just one cell (l) is

$$H_i(l) = [\mathbf{0},\ \mathbf{0}, \cdots, \cdots\ \mathbf{B}_i\ \cdots, \mathbf{0}, \cdots]\,\Delta\mathbf{R}_{cryst}\ , \tag{2.9}$$

where each $\mathbf{0}$ denotes a row vector for a cell that does not involve $H_i(l)$ and contains three zero elements for each atom in the primitive cell. The only nonzero elements are contained in $\cdots\ \mathbf{B}_i\ \cdots$ and these are positioned so they operate on the atoms in the cells which contribute to $H_i(l)$.

B. Relation of force constants for symmetrized and conventional coordinates

A potential energy containing only diagonal force constants for symmetrized coordinates is equivalent to one containing diagonal and off diagonal force constants when conventional coordinates are used. An off diagonal force constant for the symmetrized set will correspond to more than one off diagonal constant in the conventional coordinate set. Usually, the first step in a force constant fitting procedure is to approximate the diagonal force constants. Therefore, the fitting procedure may be more rapid when symmetrized coordinates are used. The force constants may also have clearer physical significances.

The relations between the symmetrized and unsymmetrized force constants are easily established by writing the potential using both sets of coordinates and then expanding the terms in the symmetrized function so it is expressed in the conventional coordinates. The X_2Y example shows how this is accomplished. The potential function in terms of conventional and symmetrized coordinates is given by

conventional:

$$V = \tfrac{1}{2}\{F_r[\Delta r(1,3)^2 + \Delta r(2,3)^2] + F_\phi\,\Delta\phi^2 + 2f_{r\phi}\,\Delta\phi[\Delta r(1,3) + \Delta r(2,3)] + 2f_{rr}\,\Delta r(1,3)\,\Delta r(2,3)\}\ ; \tag{2.10}$$

symmetrized:

$$V = \tfrac{1}{2}\{F_{sy,st}[\Delta r(1,3) + \Delta r(2,3)]^2 + F_\phi\,\Delta\phi^2 + F_{as,st}[\Delta r(1,3) - \Delta r(2,3)]^2 + 2f_{sy,\phi}\,\Delta\phi[\Delta r(1,3) + \Delta r(2,3)]\}\ . \tag{2.11}$$

When the terms in Eq. (2.11) are expanded and compared with those in Eq. (2.10) the result is

$$F_{sy,st} = \tfrac{1}{2}(F_r + f_{rr})\ ,\quad F_{sy,st} + F_{as,st} = F_r\ ,$$
$$F_{as,st} = \tfrac{1}{2}(F_r - f_{rr})\ ,\quad F_{sy,st} - F_{as,st} = f_{rr}\ , \tag{2.12}$$
$$F_{sy,\phi} = f_{r\phi}\ .$$

III. RELATIVE MOTION COORDINATES

A. General procedures

Relative motion coordinates bind groups of strongly bonded atoms which are connected by relatively weak

forces. They are defined in terms of relative translational, and relative rotational displacements of the interacting groups.

If there are N groups interacting there will be $3N$ linearly independent translation coordinates. However, three of these correspond to pure translations of the entire set of interacting groups along each of the Cartesian axes for the set. They are excluded from the coordinates used in the potential energy. The remaining $3N-3$ relative translation coordinates can be chosen so that their projection operators are orthogonal to those for the pure translations. In this way the coordinates contribute terms to the potential energy which are translationally invariant.

The number of relative rotation coordinates depends on the structures of the individual groups. If every group contains atoms in nonlinear configurations so that rotations about all axes can be defined there will be $3N$ relative rotation coordinates. If some groups contain linear atom configurations rotations about these lines can not occur. This reduces the number of relative rotation coordinates below $3N$. Finally, if all groups are in a line one relative rotation coordinate will correspond to a pure rotation about this line and will be excluded.

These situations cause no problems in determining sets of coordinates. However, of the $3N-3$ relative translation coordinates there will be three (two if the groups are in a line) which correspond to displacement patterns generated by rotational displacements of the entire set about the x, y, and z axes. In addition, there is a one to one correspondence between these coordinates and three (two if there is a linear array of groups) relative rotation coordinates about these axes. None of these relative rotation or relative translations is, by itself, orthogonal to pure crystal rotations. However, they can be coupled in pairs in the potential energy to satisfy rotational invariance.

All of the remaining coordinates may be defined so they are orthogonal to pure translations and rotations of the groups. They then ensure an invariant potential.

B. Coordinate definitions and projection operators

1. *Coordinates and operators for individual groups*

The operators which project out the relative motion coordinates from arbitrary displacements of all the atoms in the set of interacting groups are defined in terms of operators which project translational and rotational displacements of individual groups from arbitrary displacements of the atoms in the groups. The expressions for these operators are obtained in terms of axes x, y, and z within each group which are parallel to the axes for the entire set. To ensure that the operators for the group translations and rotations are orthogonal, the axes within each group are located at an origin chosen to satisfy the conditions

$$\sum_\nu x_\nu = 0\ ,\quad \sum_\nu y_\nu = 0\ ,\quad \sum_\nu z_\nu = 0\ . \tag{3.1}$$

where x_ν, y_ν, and z_ν are the positions of atom ν in the group. It is useful to begin by determining the operators which project out translations along, and rotations about, arbitrary directions. The translation operator is easily obtained. Let t denote a translation of the entire group

$$\mathbf{t} = t[\mathbf{i}\hat{t}_x + \mathbf{j}\hat{t}_y + \mathbf{k}\hat{t}_z]\ . \tag{3.2}$$

Let $(\Delta\mathbf{r})_{tr}$ denote a column vector containing the displacements of all the atoms which are induced by the group translation t. Since all atoms experience the same translation t, $(\Delta\mathbf{r})_{tr}$ may be written

$$(\Delta\mathbf{r})_{tr} = \begin{bmatrix} \Delta\mathbf{r}_1 \\ \Delta\mathbf{r}_2 \\ \vdots \\ \Delta\mathbf{r}_\nu \\ \vdots \\ \Delta\mathbf{r}_n \end{bmatrix}_{tr} = t[\hat{\mathbf{t}}]\ ,\quad \hat{\mathbf{t}} = \begin{bmatrix} \hat{t}_x \\ \hat{t}_y \\ \hat{t}_z \end{bmatrix}\ , \tag{3.3}$$

where the subscript tr denotes displacements generated by a pure translation, and $[\hat{\mathbf{t}}]$ denotes a column matrix in which the three element column matrix $\hat{\mathbf{t}}$ appears n *times*, once for each atom in the group. The elements in $\hat{\mathbf{t}}$ are seen from Eq. (3.2) to be the components of the unit vector $\hat{\mathbf{t}}$ along t, while t is the magnitude of t.

To obtain the projector for $(\Delta\mathbf{r})_{tr}$ we note that an arbitrary displacement of all the atoms in the group can be expressed as the sum of orthogonal contributions from pure translations, pure rotations, and internal displacements. Then

$$\Delta\mathbf{r} = (\Delta\mathbf{r})_{tr} + (\Delta\mathbf{r})_{rot} + (\Delta\mathbf{r})_{int}\ , \tag{3.4}$$

where $\Delta\mathbf{r}$ denotes a column vector like that in Eq. (2.2) in which the elements are the arbitrary displacements of the atoms in the group. The subscripted terms on the right-hand side give the contributions from the translational, rotational, and internal displacements, respectively. If Eq. (3.3) is used to express $(\Delta\mathbf{r})_{tr}$ the result is

$$\Delta\mathbf{r} = t[\hat{\mathbf{t}}] + (\Delta\mathbf{r})_{rot} + (\Delta\mathbf{r})_{int}\ . \tag{3.5}$$

If Eq. (3.5) is operated on from the left by $[\hat{\mathbf{t}}]^T$ and account is taken of the orthogonalities to the rotational and internal displacements the result is

$$[\hat{\mathbf{t}}]^T \Delta\mathbf{r} = nt\ ,$$

where n is the number of atoms in the group. Finally,

$$(1/n)[\hat{\mathbf{t}}]^T \Delta\mathbf{r} = t\ . \tag{3.6}$$

From Eq. (3.6) it is seen that the operator which projects t out of the arbitrary displacements of the atoms in the group is

$$\mathbf{b}_t = (1/n)[\hat{\mathbf{t}}]^T \tag{3.7}$$

The projector for a pure rotation is found by considering the equation for $(\Delta\mathbf{r})_{rot}$. Let θ denote a rotational displacement of the group about an axis through the origin of the group axes and directed along the vector $\boldsymbol{\theta}$,

$$\boldsymbol{\theta} = \theta[\mathbf{i}\hat{\theta}_x + \mathbf{j}\hat{\theta}_y + \mathbf{k}\hat{\theta}_z]\ . \tag{3.8}$$

The rotation θ induces a displacement $\Delta\mathbf{r}_\nu$ of atom ν

given by

$$\Delta \mathbf{r}_\nu = \theta \times \mathbf{r}_\nu = -\mathbf{r}_\nu \times \theta \ . \tag{3.9}$$

The matrix form for Eq. (3.9) is

$$\Delta \mathbf{r}_\nu = \begin{bmatrix} \Delta x_\nu \\ \Delta y_\nu \\ \Delta z_\nu \end{bmatrix}_{\rm rot} = \theta \mathbf{r}_\nu \hat{\theta} \ , \tag{3.10}$$

$$\mathbf{r}_\nu = \begin{bmatrix} 0 & z_\nu & -y_\nu \\ -z_\nu & 0 & x_\nu \\ y_\nu & -x_\nu & 0 \end{bmatrix} \ , \quad \hat{\theta} = \begin{bmatrix} \hat{\theta}_x \\ \hat{\theta}_y \\ \hat{\theta}_z \end{bmatrix} . \tag{3.11}$$

The equation for the displacements experienced by all the atoms due to the rotation is

$$(\Delta \mathbf{r})_{\rm rot} = \theta \, \mathbf{r} \hat{\theta} \ , \tag{3.12}$$

$$\mathbf{r} = \begin{bmatrix} \mathbf{r}_1 \\ \mathbf{r}_2 \\ \vdots \\ \mathbf{r}_\nu \\ \vdots \\ \mathbf{r}_n \end{bmatrix} . \tag{3.13}$$

When Eq. (3.12) is used in Eq. (3.5) the result is

$$\Delta \mathbf{r} = t[\hat{\mathbf{t}}] + \theta \, \mathbf{r} \hat{\theta} + (\Delta \mathbf{r})_{\rm int} \ . \tag{3.14}$$

If the atoms in the group are not all in a line $\mathbf{r}^T\mathbf{r}$ has an inverse. Then Eq. (3.14) can be operated on from the left first by $[\mathbf{r}^T\mathbf{r}]^{-1}\mathbf{r}^T$ and then by $\hat{\theta}^T$ to yield

$$\hat{\theta}^T (\mathbf{r}^T \mathbf{r})^{-1} \mathbf{r}^T \Delta \mathbf{r} = \theta \ . \tag{3.15}$$

This result holds because $\mathbf{r}^T$ is orthogonal to $[\mathbf{t}]$ by virtue of Eq. (3.1) and because the $(\Delta \mathbf{r})_{\rm int}$ term is a displacement pattern orthogonal to the first two terms in Eq. (3.4). The operator which projects θ out of $\Delta \mathbf{r}$ is then

$$\mathbf{b}_\theta = \hat{\theta}^T (\mathbf{r}^T \mathbf{r})^{-1} \mathbf{r}^T \ . \tag{3.16}$$

If the atoms in the group are on one line $\mathbf{r}^T\mathbf{r}$ is a 3×3 singular matrix because rotations about this line are not defined. In this case θ must be restricted to directions in the plane normal to the line of nuclei and $\mathbf{r}$ will be restricted to the two columns associated with rotations about the two axes normal to the internuclear line. Then $\mathbf{r}^T\mathbf{r}$ is a 2×2 matrix which can be inverted so that with this understanding Eq. (3.16) still applies.

In this work Eq. (3.16) is used to define the operators for relative rotation coordinates which are orthogonal to the pure translations. Equation (3.16) has been derived on the assumption that these coordinates are to be defined in terms of rotations about axes parallel to those for the entire set of interacting groups. Cases may occur, however, where a better choice is to use group rotations about axes appropriate to the group symmetry which may be inclined to the axes for the entire set. When the final set of symmetrized coordinates is defined using these relative rotations the operators can be converted into operators appropriate to the axes for the entire set by using equations analogous to Eq. (2.8) to resolve the components for each group along the axes for the set. This means employing a different projection matrix for each group in the analog to the **A** matrix in Eq. (2.5b).

The illustrative application in Sec. V, and the application to trigonal selenium in the accompanying paper, employ only relative rotations about axes parallel to those for the set. This appears to be a common possibility in practice and these applications display the essential features of our method quite simply.

2. *Operators for relative motion coordinates*

a. General comments. The projectors for those relative translation and relative rotation coordinates which are not orthogonal to pure rotations of the interacting groups are obtained from the expressions for displacements induced by rotations of the groups considered as a rigid unit. It is useful to begin by expressing the arbitrary displacements of all the atoms in all the groups in the form

$$(\Delta \mathbf{r})_{\rm set} = (\Delta \mathbf{r})_{g,\rm tr} + (\Delta \mathbf{r})_{g,\rm rot} + (\Delta \mathbf{r})_{g,\rm int} + (\Delta \mathbf{r})_{\rm int} \ , \tag{3.17}$$

where $(\Delta \mathbf{r})_{\rm set}$ denotes a column vector with the displacements of all the atoms as components. It may be subdivided conveniently in the form

$$(\Delta \mathbf{r})_{\rm set} = \begin{bmatrix} \Delta \mathbf{r}(1) \\ \vdots \\ \Delta \mathbf{r}(i) \\ \vdots \\ \Delta \mathbf{r}(N) \end{bmatrix} , \tag{3.18}$$

where $\Delta \mathbf{r}(i)$ is a column vector containing the displacements of the atoms in group i as elements. The $(\Delta \mathbf{r})_{g,\rm tr}$ and $(\Delta \mathbf{r})_{g,\rm rot}$ in Eq. (3.17) are column vectors containing the displacements of the atoms which are induced by a pure translation of the entire set, and a pure rotation of the set, respectively. If the axes for the set have their origin located to satisfy constraints analogous to those in Eq. (3.1), the $(\Delta \mathbf{r})_{g,\rm rot}$ will be orthogonal to $(\Delta \mathbf{r})_{g,\rm tr}$. The consstraints are

$$\sum_i x(i) = 0, \quad \sum_i y(i) = 0, \quad \sum_i z(i) = 0 \ , \tag{3.19}$$

where $x(i)$, $y(i)$, and $z(i)$ are the positions of the origin of the axes in group i relative to the origin of the axes for the set.

The third term in Eq. (3.17), $(\Delta \mathbf{r})_{g,\rm int}$, is made up of displacements induced by translations and rotations of the individual groups treated as rigid units. These can always be constructed so that $(\Delta \mathbf{r})_{g,\rm int}$ is orthogonal to the first two terms. Finally, the last term is composed of displacements of the atoms *within* the groups which are chosen so they are orthogonal to $(\Delta \mathbf{r})_{g,\rm int}$ and, therefore, to the first two terms also.

It is clear that $(\Delta \mathbf{r})_{g,\rm tr}$ can be expressed by

$$(\Delta \mathbf{r})_{g,\rm tr} = t[\hat{\mathbf{t}}]_g \ , \tag{3.20}$$

where $[\hat{\mathbf{t}}]_g$ contains the $[\hat{\mathbf{t}}(i)]$ for each group i defined as in Eq. (3.3) all in a column. However, in Eq. (3.20) the $\hat{\mathbf{t}}$ is the same for every group because they all move in the same direction.

The equation for $(\Delta\mathbf{r})_{g,\mathrm{rot}}$ is obtained by considering the equation for the displacement $[\Delta\mathbf{r}_\nu(i)]_{g,\mathrm{rot}}$ of atom ν in group i which is induced by a rigid rotation of the entire set:

$$\Delta\mathbf{r}_\nu(i) = \theta \times [\mathbf{a}(i) + \mathbf{r}_\nu(i)] \ . \tag{3.21}$$

Equation (3.21) is like Eq. (3.9) except that the vector $\mathbf{a}(i)$ from the origin of the set to the origin of the group i appears. When Eq. (3.21) is put into matrix form the result is

$$[\Delta\mathbf{r}_\nu(i)]_{g,\mathrm{rot}} = \theta(\mathbf{R}(i) + \mathbf{r}(i))\,\hat{\theta} \ , \tag{3.22}$$

where $\mathbf{r}_\nu(i)$ is defined for atom ν in group i as in Eq. (3.11). $\mathbf{R}(i)$ is defined in the same way as $\mathbf{r}_\nu$ in Eq. (3.11):

$$\mathbf{R}(i) = \begin{bmatrix} 0 & z(i) & -y(i) \\ -z(i) & 0 & x(i) \\ y(i) & -x(i) & 0 \end{bmatrix} \ . \tag{3.23}$$

Finally, if $[\Delta\mathbf{r}(i)]_{g,\mathrm{rot}}$ denotes the displacements of all the atoms in group i due to the pure rotation

$$[\Delta\mathbf{r}(i)]_{g,\mathrm{rot}} = \theta\,([\mathbf{R}(i)] + \mathbf{r}(i))\,\hat{\theta} \ , \tag{3.24}$$

where $\mathbf{r}(i)$ is the same as in Eq. (3.13) and $[\mathbf{R}(i)]$ denotes a column of the $\mathbf{R}(i)$ matrices which appears once for each atom in group i. With these ideas in mind the equation for $(\Delta\mathbf{r})_{g,\mathrm{rot}}$ becomes

$$(\Delta\mathbf{r})_{g,\mathrm{rot}} = \theta[\mathbf{R}]_g\,\hat{\theta} + \theta[\mathbf{r}]\,\hat{\theta} \ , \tag{3.25}$$

where $[\mathbf{R}]_g$ denotes a column containing the $[\mathbf{R}(i)]$ from Eq. (3.24) and $[\mathbf{r}]$ denotes a column of $\mathbf{r}(i)$.

b. Projection operators for relative translation coordinates. The projectors for the three (or two) relative translation coordinates which are not orthogonal to pure rotations can be expressed in terms of the elements in $[\mathbf{R}]_g$. First the operator which projects θ out of $(\Delta\mathbf{r})_{\mathrm{set}}$ is determined in such a form that it is orthogonal to $[\hat{\mathbf{t}}]_g$ in Eq. (3.20). The form is

$$\mathbf{b}_{R\theta} = [\mathbf{b}_{R\theta}(1), \ldots, \mathbf{b}_{R\theta}(i), \ldots, \mathbf{b}_{R\theta}(N)] \ , \tag{3.26}$$

$$\mathbf{b}_{R\theta}(i) = \hat{\theta}^T \Big(\sum_j \mathbf{R}^T(j)\,\mathbf{R}(j) \Big)^{-1} \frac{[\mathbf{R}(i)]^T}{n(i)} \ . \tag{3.27}$$

In Eq. (3.27), $n(i)$ denotes the number of atoms in group i and the other symbols are defined in Eq. (3.24).

Using the definitions in Eqs. (3.26) and (3.27) together with the conditions in Eqs. (3.1) and (3.19), it is seen that

$$\mathbf{b}_{R\theta}(\Delta\mathbf{r})_{\mathrm{set}} = \mathbf{b}_{R\theta}[\mathbf{R}]_g\,\hat{\theta}\theta = \hat{\theta}^T \Big(\Big(\sum_j \mathbf{R}(j)^T\,\mathbf{R}(j) \Big)^{-1} \Big) \Big(\sum_i \mathbf{R}(i)^T\,\mathbf{R}(i) \Big)\,\hat{\theta}\theta = \theta \ .$$

Using Eq. (3.26), it is possible to define three (or two) operators which project out the three (or two) relative translation coordinates which are not orthogonal to pure rotations about the x, y, or z axes. Denoting x, y, or z by α, and the unit vectors i, j, and k by $\hat{\alpha}$, these become

$$\mathbf{b}_{R\alpha} = [\mathbf{b}_{R\alpha}(1), \ldots, \mathbf{b}_{R\alpha}(i), \ldots, \mathbf{b}_{R\alpha}(N)] \ , \tag{3.28}$$

$$\mathbf{b}_{R\alpha}(i) = \hat{\alpha}^T \Big(\sum_j \mathbf{R}(j)^T\,\mathbf{R})\,j) \Big)^{-1} \frac{[\mathbf{R}(i)]^T}{n(i)} \ . \tag{3.29}$$

In Eq. (3.28), α denotes x, y, or z and $\hat{\alpha}^T$ denotes $[1,0,0]$, $[0,1,0]$, or $[0,0,1]$ for x, y, or z, respectively.

If the operator in Eq. (3.28) is applied to $(\Delta\mathbf{r})_{\mathrm{set}}$, the result is

$$\mathbf{b}_{R\alpha}(\Delta\mathbf{r})_{\mathrm{set}} = \mathbf{b}_{R\alpha}[\mathbf{R}]_g\,\hat{\theta}\theta = \theta\hat{\alpha}^T\,\hat{\theta} \ . \tag{3.30}$$

The operators $\mathbf{b}_{R\alpha}(i)$ have identical elements for every atom in the group. If they are looked on as defining displacements of the atoms it is seen that $\mathbf{b}_{R\alpha}(i)$ corresponds to a pure group translation. Therefore, $\mathbf{b}_{R\alpha}$ are projectors of relative translation coordinates. If the groups are all in line there are only two coordinates since $\mathbf{b}_{R\alpha}$ is not defined for the direction which coincides with the axis of rotation.

The remaining $3N-6$ ($3N-5$ for a linear array of groups) projectors for relative translation coordinates are conveniently determined by choosing symmetrized stretch coordinates derived by considering translational displacements of the groups along the lines connecting their origins. This is exactly the same procedure as is used for obtaining symmetrized valence coordinates based on interatomic stretches. The projectors for these coordinates are obtained using Eq. (3.7) with $\hat{\mathbf{t}}$ chosen so that $\hat{\mathbf{t}}$ points along the line between the groups for which the stretch projector is to be defined. The procedure for doing this is illustrated in Sec. V and in the accompanying paper on trigonal selenium.

c. Projectors for relative rotation coordinates. The $\mathbf{b}_{r\alpha}$ for the relative rotation coordinates which are not orthogonal to pure rotations can be found by the same procedure as for the $\mathbf{b}_{R\alpha}$. The operators are

$$\mathbf{b}_{r\alpha} = (\mathbf{b}_{r\alpha}(1), \ldots, \mathbf{b}_{r\alpha}(i), \ldots, \mathbf{b}_{r\alpha}(N)) \ , \tag{3.31}$$

$$\mathbf{b}_{r\alpha}(i) = \hat{\alpha}^T([\mathbf{r}]^T[\mathbf{r}])^{-1}\mathbf{r}(i)^T \ . \tag{3.32}$$

Equations (3.31) and (3.32) are such that the constraints in Eq. (3.1) yield

$$\mathbf{b}_{r\alpha}(\Delta\mathbf{r})_{\mathrm{set}} = \mathbf{b}_{r\alpha}[\mathbf{r}]\,\hat{\theta}\theta = \theta\hat{\alpha}^T\,\hat{\theta} \ . \tag{3.33}$$

If all the groups are in one line the $\mathbf{b}_{r\alpha}$ for α along this line corresponds to a pure rotation. This coordinate is not used in the potential. The corresponding $\mathbf{b}_{R\alpha}$ vanishes.

The remaining relative rotation coordinates are obtained by using Eq. (3.16) to define operators for rotations of adjacent groups about parallel axes in opposite directions of rotation. Such coordinates will be orthogonal to those defined by the projectors in Eqs. (3.28) and (3.31). Symmetrized relative rotations may be obtained by applying group theory projection techniques to coordinates defined in this way. This is illustrated in what follows and in the application to trigonal selenium.

IV. ROTATIONAL INVARIANCE CONDITIONS

The only coordinates which do not satisfy rotational invariance are those with the projectors $\mathbf{b}_{R\alpha}$ and $\mathbf{b}_{r\alpha}$. The contribution of each α pair to the potential is

$$\Delta V = \tfrac{1}{2}\,(F_r H_{r\alpha}^2 + F_{R\alpha} H_{R\alpha}^2 + 2f_{r\alpha,R\alpha} H_{r\alpha} H_{R\alpha}) \ . \qquad (4.1)$$

Equation (3.30) expressed the excitation $H_{R\alpha}$ by arbitrary atom displacements and Eq. (3.33) gives the excitation $H_{r\alpha}$. When these are used in Eq. (4.1) the result is

$$\Delta V = \tfrac{1}{2}\,\theta^2[\hat{\alpha}^T\,\hat{\theta}]^2\,(F_{r\alpha} + F_{R\alpha} + 2f_{r\alpha,R\alpha}) \ .$$

Rotational invariance is assured if

$$f_{r\alpha,R\alpha} = -\tfrac{1}{2}\,(F_{r\alpha} + F_{R\alpha}) \ . \qquad (4.2)$$

Couplings of coordinates $H_{R\alpha} H_{r\beta}$ with $\beta \neq \alpha$ must be excluded if Eq. (4.2) is to apply.

V. ILLUSTRATIVE EXAMPLE FOR RELATIVE MOTION COORDINATES

The accompanying paper on trigonal selenium derives relative motion coordinates for the simple, but important, special case of two interacting groups. To illustrate a more general possibility coordinates for three interacting groups disposed in a nonlinear array are given here. We emphasize that these coordinates give only that part of the potential associated with interactions among the groups. This means, for example, that if the three groups were all in the same primitive cell of a crystal the coordinates would not suffice for explaining the crystal potential. Additional coordinates would be needed to express interactions between groups (or atoms) in adjacent primitive cells.

The groups will be assumed to have C_{2v} symmetry with group 3 being at the apex of a triangle and groups 1 and 2 located at the corners. The z axis is the symmetry axis and is directed out from the triangle. The y axis is the plane of the groups and is directed parallel to the vector from group 2 to group 1. Groups 1 and 2 will contain two atoms and group 3, three atoms. The positions are

group 1: $x_1(1)=0,\quad y_1(1)=+c,\quad z_1(1)=0,$
$x_2(1)=0,\quad y_2(1)=-c,\quad z_2(1)=0;$

group 2: $x_1(2)=0,\quad y_1(2)=-c,\quad z_1(2)=0,$
$x_2(2)=0,\quad y_2(2)=+c,\quad z_2(2)=0;$

group 3: $x_1(3)=d,\quad y_1(3)=0,\quad z_1(3)=0,$
$x_2(3)=-d,\quad y_2(3)=0,\quad z_2(3)=0,$
$x_3(3)=0,\quad y_3(3)=0,\quad z_3(3)=0.$

The positions of the groups are

$$x(1)=0,\quad y(1)=D,\quad z(1)=-\tfrac{1}{2}\,C,$$
$$x(2)=0,\quad y(2)=-D,\quad z(2)=-\tfrac{1}{2}\,C,$$
$$x(3)=0,\quad y(3)=0,\quad z(3)=C.$$

Using these data the matrices in Eqs. (3.11) and (3.23) are

$$\mathbf{r}_1(1)=\begin{bmatrix}0&0&-c\\0&0&0\\c&0&0\end{bmatrix},\quad \mathbf{r}_2(1)=-\mathbf{r}_1(1).\qquad \mathbf{r}_1(2)=-\mathbf{r}_1(1)\ ,\quad \mathbf{r}_2(2)=\mathbf{r}_1(1)\ ;$$

$$\mathbf{r}_1(3)=\begin{bmatrix}0&0&0\\0&0&d\\0&-d&0\end{bmatrix},\quad \mathbf{r}_2(3)=-\mathbf{r}_1(3),\quad \mathbf{r}_3(3)=\begin{bmatrix}0&0&0\\0&0&0\\0&0&0\end{bmatrix};$$

$$\mathbf{R}(1)=\begin{bmatrix}0&-\frac{1}{2}C&-D\\\frac{1}{2}C&0&0\\D&0&0\end{bmatrix},\quad \mathbf{R}(2)=\begin{bmatrix}0&-\frac{1}{2}C&D\\\frac{1}{2}C&0&0\\-D&0&0\end{bmatrix},$$

$$\mathbf{R}(3)=\begin{bmatrix}0&C&0\\-C&0&0\\0&0&0\end{bmatrix}.$$

The $\mathbf{b}_{R\alpha}(i)$ defined in Eq. (3.29) are

$$\mathbf{b}_{Rx}(1)=C_{Rx}\tfrac{1}{2}\,[0,\tfrac{1}{2}C,D,0,\tfrac{1}{2}C,D],$$
$$\mathbf{b}_{Rx}(2)=C_{Rx}\tfrac{1}{2}\,[0,\tfrac{1}{2}C,-D,0,\tfrac{1}{2}C,-D]\ ;$$
$$\mathbf{b}_{Rx}(3)=C_{Rx}\tfrac{1}{3}\,[0,-C,0,0,-C,0,0,-C,0]\ ,$$
$$C_{Rx}=1/(\tfrac{3}{2}\,C^2+2D^2)\ ;$$
$$\mathbf{b}_{Ry}(1)=C_{Ry}\tfrac{1}{2}\,[-\tfrac{1}{2}C,0,0,-\tfrac{1}{2}C,0,0]\ ,$$
$$\mathbf{b}_{Ry}(2)=\mathbf{b}_{Ry}(1)\ ;$$
$$\mathbf{b}_{Ry}(3)=C_{Ry}\tfrac{1}{3}[C,0,0,C,0,0,C,0,0],\quad C_{Ry}=2/3C^2\ ;$$
$$\mathbf{b}_{Rz}(1)=C_{Rz}\tfrac{1}{2}\,[-D,0,0,-D,0,0],\quad \mathbf{b}_{Rz}(2)=-\mathbf{b}_{Rz}(1)\ ;$$
$$\mathbf{b}_{Rz}(3)=[0,0,0,0,0,0,0,0,0],\quad C_{Rz}=1/2D^2\ .$$

It is clear that the $\mathbf{b}_{R\alpha}$ constructed according to Eq. (3.28) using these definitions are orthogonal to the $[\hat{\mathbf{t}}]_g$ in Eq. (3.20) and, because of Eq. (3.1) to the $[\mathbf{r}]$ in Eq. (3.25).

Three symmetrized relative translation coordinates with $\mathbf{b}_{t\alpha}$ projectors orthogonal to the $\mathbf{b}_{R\alpha}$ and to $[\mathbf{t}]_g$ remain to be defined. They can be obtained by following procedures exactly like those used for obtaining symmetric stretch coordinates among atoms. In this case two coordinates can be the symmetric and antisymmetric stretches involving all three groups and the third can be the stretch between groups 1 and 2. These coordinates can be defined using appropriate forms for the operators in Eq. (3.7). To obtain the symmetric and antisymmetric stretches the stretch between groups 1 and 3 can be projected. The stretch between groups 1 and 3 uses $\hat{\mathbf{t}}^T$ given by

$$\hat{\mathbf{t}}^T=[0,\ \sin\varphi,\ -\cos\varphi]\ .$$

Here φ is half the apex angle of the triangle of groups. The operator for this stretch is

$$\mathbf{b}_{1,3}=[\mathbf{b}_{1,3}(1),\ 0,\ -\mathbf{b}_{1,3}(3)]\ ,$$

where 0 is a row vector with six zero elements, and

$$\mathbf{b}_{1,3}(1)=\tfrac{1}{2}[\hat{t}^T,\hat{t}^T]\ ,$$
$$\mathbf{b}_{1,3}(3)=\tfrac{1}{3}[\hat{t}^T,\hat{t}^T,\hat{t}^T]\ .$$

Projection leads to the two coordinates

$$\mathbf{b}_{sy,st}=[\mathbf{b}_{1,3}(1),\ \mathbf{b}_{2,3}(2),\ -(\mathbf{b}_{1,3}(3)+\mathbf{b}_{2,3}(3))]\ ,$$
$$\mathbf{b}_{as,st}=[\mathbf{b}_{1,3}(1),\ -\mathbf{b}_{2,3}(2),\ -(\mathbf{b}_{1,3}(3)-\mathbf{b}_{2,3}(3))]\ .$$

The $\mathbf{b}_{2,3}(2)$ and $\mathbf{b}_{2,3}(3)$ are like $\mathbf{b}_{1,2}(1)$ and $\mathbf{b}_{1,3}(3)$, respectively, except for using

$$\hat{\mathbf{t}}^T = [0, -\sin\varphi, -\cos\varphi] .$$

The remaining coordinate uses the projector

$$\mathbf{b}_{1,2} = [\mathbf{b}_{1,2}(1), -\mathbf{b}_{1,2}(2), 0] ,$$

where 0 is a row vector with nine zero elements. In these projectors $\hat{\mathbf{t}}^T$ is just

$$\hat{\mathbf{t}}^T = [0, 1, 0] ,$$

$$\mathbf{b}_{1,2}(1) = \tfrac{1}{2}[0, 1, 0, 0, 1, 0], \quad \mathbf{b}_{1,2}(2) = \mathbf{b}_{1,2}(1) .$$

The three $\mathbf{b}_{r\alpha}$ projectors defined using Eqs. (3.31) and (3.32) are easily obtained

$$\mathbf{b}_{rx} = (1/4c^2)[0, 0, c, 0, 0, -c, 0, 0, -c, 0, 0, c, 0, 0, 0, 0, 0, 0, 0, 0] ,$$

$$\mathbf{b}_{ry} = (1/2d^2)[0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, -d, 0, 0, d, 0, 0, 0] ,$$

$$\mathbf{b}_{rz} = [1/(4c^2 + 2d^2)][-c, 0, 0, c, 0, 0, c, 0, 0, -c, 0, 0, 0, d, 0, 0, -d, 0, 0, 0, 0] .$$

There remain three coordinates involving relative rotations to determine. The projectors must be orthogonal to the $\mathbf{b}_{r\alpha}$ projectors. They can be found by analogous procedures to those used for obtaining the final relative translation coordinates. The operators in Eq. (3.16) are used for this purpose. We begin by defining a coordinate in which groups 1 and 3 rotate by equal and opposite amounts about the z direction. To avoid a too cumbersome notation this coordinate will be simply designated as $\mathbf{b}_r$. Then

$$\mathbf{b}_r = [\mathbf{b}_r(1), 0, -\mathbf{b}_r(3)] ,$$

$$\mathbf{b}_r(1) = (1/2c^2)[-c, 0, 0, c, 0, 0] ,$$

$$\mathbf{b}_r(3) = (1/2d^2)[0, d, 0, 0, -d, 0, 0, 0, 0] .$$

Projection yields the symmetrized rotations

$$\mathbf{b}_{r,sy} = [\mathbf{b}_r(1), \mathbf{b}_r(2), -2\mathbf{b}_r(3)] ,$$

$$\mathbf{b}_{r,as} = [\mathbf{b}_r(1), -\mathbf{b}_r(2), 0] ,$$

where 0 is a row vector with nine zero elements, and

$$\mathbf{b}_r(2) = (1/2c^2)[c, 0, 0, -c, 0, 0] .$$

The third coordinate is the counter rotation of groups 1 and 2 about their x axes. Denoting it by $\mathbf{b}_{r3}$, the projector is

$$\mathbf{b}_{r3} = [\mathbf{b}_{r3}(1), -\mathbf{b}_{r3}(2), 0] ,$$

0 is a row vector with nine zero elements, and

$$\mathbf{b}_{r3}(1) = (1/2c^2)[0, 0, c, 0, 0, -c] ,$$

$$\mathbf{b}_{r3}(2) = (1/2c^2)[0, 0, -c, 0, 0, c] .$$

With these definitions it is seen that $\mathbf{b}_{r,sy}$, $\mathbf{b}_{r,as}$, and $\mathbf{b}_{r3}$ are all orthogonal to the $\mathbf{b}_{r\alpha}$.

The coordinates belong to the representations of C_{2v} in the following ways:

A_1: $\mathbf{b}_{sy,st}$, $\mathbf{b}_{1,2}$;

A_2: $\mathbf{b}_{Rz}$, $\mathbf{b}_{rz}$, $\mathbf{b}_{r,sy}$;

B_1: $\mathbf{b}_{Rx}$, $\mathbf{b}_{rx}$, $\mathbf{b}_{as,st}$, $\mathbf{b}_{r3}$;

B_2: $\mathbf{b}_{Ry}$, $\mathbf{b}_{ry}$, $\mathbf{b}_{r,as}$.

The projectors of B_1 symmetry are symmetric under reflection in the yz plane.

The three pure translations along x, y, and z are not included as coordinates. These motions do not induce changes in the geometric configuration of the groups and, therefore, cannot produce a change in potential energy due to intergroup interaction.

VI. SECULAR EQUATION: GENERAL COMMENTS

The Born–von Kármán treatment of crystal dynamics expresses the normal modes of the entire crystal in terms of modes for a single primitive cell. The atoms in every other cell vibrate in exactly the same patterns, the motions differing only in phase from cell to cell. The phases are determined by the wave vector κ which is defined in terms of the usual reciprocal vectors $\mathbf{b}_1$, $\mathbf{b}_2$, and $\mathbf{b}_3$ by

$$\kappa = 2\pi(f_1\mathbf{b}_1 + f_2\mathbf{b}_2 + f_3\mathbf{b}_3) .$$

The $\mathbf{b}_i$ are related to the primitive translation vectors $\mathbf{a}_1$, $\mathbf{a}_2$, and $\mathbf{a}_3$ by

$$\mathbf{b}_i = (\mathbf{a}_j \times \mathbf{a}_k)/(\mathbf{a}_i \cdot \mathbf{a}_j \times \mathbf{a}_k) ,$$

where i, j, k denote indices 1, 2, 3 which go in cyclic order. The f_i can take on continuous values in the range

$$0 \leq f_i \leq 1 .$$

Any triplet of values f_1, f_2, f_3 defines a particular κ and $3n$ normal modes can be found for this κ (n is the number of atoms in a primitive cell). During any normal mode the atoms in the primitive cell at

$$\mathbf{R}(l) = l_1\mathbf{a}_1 + l_2\mathbf{a}_2 + l_3\mathbf{a}_3$$

move in such a way that

$$\Delta\mathbf{R}(\nu, l, t) = \Delta\mathbf{R}(\nu, 0, t)\exp[i\kappa \cdot \mathbf{R}(l)] .$$

In these relations $\Delta\mathbf{R}(\nu, l, t)$ denotes the displacement of atom ν in cell l at time t and $\Delta\mathbf{R}(\nu, 0, t)$ is the displacement of the same atom in the origin cell at time t.

It is convenient to derive the secular equation by expressing displacements in mass adjusted coordinates $\mathbf{q}_\nu = m_\nu^{1/2}\Delta\mathbf{R}_\nu$. The next step is to express the column vector $\mathbf{q}$, which contains the $\mathbf{q}_\nu$, as a linear combination of mass adjusted basis vectors which belong to the group of the wave vector κ. Thus, if a primitive cell contains n atoms it is possible to express the vector $\mathbf{q}$ in the form

$$\mathbf{q} = \sum_i \hat{\mathbf{L}}_i w_i = \hat{\mathbf{L}}\mathbf{w} \tag{6.1}$$

where each $\hat{\mathbf{L}}_i$ denotes a normalized column vector with $3n$ elements, three for each atom. The w_i are the components of $\mathbf{q}$ in the basis $\hat{\mathbf{L}}$. The basis vector $\hat{\mathbf{L}}_i$ may be obtained by applying the group theory projection operators appropriate to the group of the wave vector to the displacements of individual atoms, or combinations of atom displacements.

In the case of molecular crystals it is useful to begin by defining a set of basis vectors for each molecule in the primitive cell. These may then be subjected to the

group theory projection operators to produce a basis set for the group of the wave vector. It is possible to define the basis vectors for each molecule so that three vectors are associated with pure translations, three with pure rotations and the remaining with internal displacement patterns. One of the writers has used this procedure for calculating normal modes of large molecules.[13]

With this in mind the basis vectors for a single molecule are written in the form

$$\hat{L} = [\hat{L}_{\bar{X}}, \hat{L}_{\bar{Y}}, \hat{L}_{\bar{Z}}, \hat{L}_{r\bar{X}}, \hat{L}_{r\bar{Y}}, \hat{L}_{r\bar{Z}}, \hat{L}_1, \hat{L}_2, \ldots, \hat{L}_{3n-6}] \ . \quad (6.2)$$

The $\hat{L}_{\bar{X}}$, $\hat{L}_{\bar{Y}}$, and $\hat{L}_{\bar{Z}}$, are obtained by converting the column vector developed from pure translations along X, Y, and Z to mass adjusted components. Similarly, the displacements generated by pure rotations are mass adjusted to obtain the $\hat{L}_{r\bar{X}}$, etc. In the case of the rotational displacements it is necessary that the axes in the molecule have their origin at the center of mass [hence the bars in the $\bar{X}$, etc., in Eq. (6.2)]. They are taken parallel to the crystal axes. The remaining basis vectors can be obtained by considering internal displacement patterns which are linearly independent. If, as is true in many hydrocarbons, some displacement patterns are resisted by strong forces and others by relatively weak forces, the basis vectors can be chosen to express these situations. This assists in approximations which include couplings between low frequency intramolecular modes and modes involving relative molecular motions in the crystal. These displacement patterns are mass adjusted and the entire set is subjected to a Schmidt orthogonalization process beginning with the first three and proceeding on in such a way that the internal vectors are orthogonalized last. This ensures that the first six vectors are associated with pure translational and rotational motions of the molecule considered as a rigid body.

Again, if $\bar{\alpha}$ denotes $\bar{X}$, $\bar{Y}$, or $\bar{Z}$ the forms of the first six vectors in Eq. (6.2) are

$$\mathbf{L}_{\bar{\alpha}} = M^{-1/2} \begin{bmatrix} \mathbf{L}_{\bar{\alpha}_1} \\ \vdots \\ \mathbf{L}_{\bar{\alpha}_\nu} \\ \vdots \\ \mathbf{L}_{\bar{\alpha}_n} \end{bmatrix} , \quad \mathbf{L}_{r\bar{\alpha}} = I_{\bar{\alpha}}^{-1/2} \begin{bmatrix} \mathbf{L}_{r\bar{\alpha}_1} \\ \vdots \\ \mathbf{L}_{r\bar{\alpha}} \\ \vdots \\ \mathbf{L}_{r\bar{\alpha}_n} \end{bmatrix} , \quad (6.3)$$

where M is the molecular mass and $I_{\bar{\alpha}}$ is the moment of intertia around $\bar{\alpha}$:

$$\mathbf{L}_{\bar{X}\nu} = m_\nu^{1/2} \begin{bmatrix} 1 \\ 0 \\ 0 \end{bmatrix} , \quad \mathbf{L}_{\bar{Y}\nu} = m_\nu^{1/2} \begin{bmatrix} 0 \\ 1 \\ 0 \end{bmatrix} , \quad \mathbf{L}_{\bar{Z}\nu} = m_\nu^{1/2} \begin{bmatrix} 0 \\ 0 \\ 1 \end{bmatrix} ,$$

$$\mathbf{L}_{r\bar{X}\nu} = m_\nu^{1/2} \begin{bmatrix} 0 \\ -\bar{Z}_\nu \\ \bar{Y}_\nu \end{bmatrix} , \quad \mathbf{L}_{r\bar{Y}\nu} = m_\nu^{1/2} \begin{bmatrix} \bar{Z}_\nu \\ 0 \\ -\bar{X}_\nu \end{bmatrix} ,$$

$$\mathbf{L}_{r\bar{Z}\nu} = m_\nu^{1/2} \begin{bmatrix} -\bar{Y}_\nu \\ \bar{X}_\nu \\ 0 \end{bmatrix} .$$

In these equations the bars over the symbols denotes that coordinates are measured from an origin at the center of mass of the molecule. Then $\bar{X}_\nu$, $\bar{Y}_\nu$, and $\bar{Z}_\nu$ denote the position of atom ν relative to the center of mass of the molecule.

The basis vectors for the entire set of molecules may be written by placing the vectors for the molecules successively down the diagonal of a large matrix. Thus,

$$\hat{L}_{\text{cell}} = \begin{bmatrix} \hat{L}(1) & & & \\ & \hat{L}(2) & & \\ & & \ddots & \\ & & & \hat{L}(m) \end{bmatrix} . \quad (6.4)$$

These vectors may be subjected to the group theory projection process to produce a set which will block diagonalizes the secular equation. In some cases the vectors may have complex components, but it can be made Hermitean. It will be assumed in what follows that $\hat{L}_{\text{cell}}$ has been formed in this manner.

The kinetic energy contributed by the atoms in one primitive cell is just

$$\tfrac{1}{2} \dot{\mathbf{q}}(l)^T \dot{\mathbf{q}}(l) = T(l) \ ,$$

$$\mathbf{q}(l) = \mathbf{q}(0) \exp(i\boldsymbol{\kappa} \cdot \mathbf{R}(l)) = \hat{\mathbf{L}}\mathbf{w} \exp[i\boldsymbol{\kappa} \cdot \mathbf{R}(l)] \ ,$$

$$\tfrac{1}{2} \dot{\mathbf{q}}(l)^T \dot{q}(l) = \dot{\mathbf{w}}^{cT} \hat{\mathbf{L}}^{cT} \mathbf{L}\dot{\mathbf{w}} = \dot{\mathbf{w}}^{cT} \mathbf{E}\dot{\mathbf{w}} \ ,$$

where $\mathbf{E}$ is the identity matrix. The kinetic energy for the entire crystal is then

$$T = \tfrac{1}{2} N \dot{\mathbf{w}}^{cT} \mathbf{E} \dot{\mathbf{w}} \ , \quad (6.5)$$

N is the number of primitive cells in the crystal.

To obtain the potential energy the excitations of the coordinates for each cell must be calculated. Let B denote a matrix composed of all the row vectors $\mathbf{B}_i$ which project the coordinates for a particular cell. Since each cell has the same coordinates the matrix B is the same for all cells. For those coordinates which express inter-cell interactions the $\mathbf{B}_i$ vectors will have elements which act on displacements of atoms in the cell l for which the coordinates are associated, together with displacements of atoms in one or more adjacent cells. If $\mathbf{H}(l)$ denotes a column vector containing as elements the excitations $H_i(l)$ of all the coordinates for cell l, $\mathbf{H}(l)$ can be expressed by[13]

$$\mathbf{H}(l) = \sum_{\tau=0} \mathbf{B}(\tau) \, \Delta\mathbf{R}(l+\tau) = \sum_{\tau} \mathbf{B}(\tau) \, \Delta\mathbf{R}(0) \exp[i\boldsymbol{\kappa} \cdot \mathbf{R}(l+\tau)]$$

$$= \mathbf{B}(\kappa) \, \Delta\mathbf{R}(0) \exp[i\boldsymbol{\kappa} \cdot \mathbf{R}(l)] \ , \quad (6.6)$$

$$\mathbf{B}(\kappa) = \sum_{\tau=0} \mathbf{B}(\tau) \exp[i\boldsymbol{\kappa} \cdot \mathbf{R}(\tau)] \ . \quad (6.7)$$

In these equations $\Delta\mathbf{R}(l+\tau)$ denotes a column vector containing the displacements of all the atoms in the cell at $\mathbf{R}(l+\tau)$. We now write

$$\mathbf{B}(\kappa) \, \Delta\mathbf{R}(0) = \mathbf{B}(\kappa) \, \mathbf{m}^{-1/2} \mathbf{q}(0) = \mathbf{D}(\kappa) \, \hat{\mathbf{L}}\mathbf{w} \ . \quad (6.8)$$

Here $\mathbf{m}^{-1/2}$ denotes a diagonal matrix in which each of the $m_\nu^{-1/2}$ appears three times in the proper location to be acted on by the components of $\mathbf{B}(\kappa)$ associated with atom ν.

The potential energy is given by

$$V = \frac{N}{2} \sum_j \mathrm{H}(0)^{cT} F_{0,j} \mathrm{H}(j)$$

$$= \frac{N}{2} \mathrm{w}^{cT} \hat{\mathrm{L}}^{cT} \mathrm{D}(\kappa)^{cT} \mathrm{F}(\kappa) \mathrm{D}(\kappa) \hat{\mathrm{L}} \mathrm{w} \ , \qquad (6.9)$$

$$\mathrm{F}(\kappa) = \sum_j F_{0,j} \exp[i\kappa \cdot \mathrm{R}(j)] \ . \qquad (6.10)$$

The secular equation is

$$|\lambda \mathrm{E} - \mathrm{M}(\kappa)| = 0 \ , \quad \mathrm{M}(\kappa) = \hat{\mathrm{L}}^{cT} \mathrm{D}(\kappa)^{cT} \mathrm{F}(\kappa) \mathrm{D}(\kappa) \hat{\mathrm{L}} \ . \qquad (6.11)$$

VII. DISCUSSION

The symmetry group for a set of valence symmetry or relative motion coordinates may not be the same as for the crystal. However, there will usually be operations in common to both symmetry groups. Coordinates which behave differently under the common operations cannot interact in the potential. Coordinates which transform in the same way under the common operations can interact in the potential even if they belong to different representations of the local group for the interacting atoms. However, if the bonding electron distributions have symmetries closely like the local symmetry these interactions should be small. It is reasonable to neglect interactions between coordinates belonging to different representations of the local symmetry group in fitting force constants.

An example of this situation is provided by the set of coordinates used for trigonal selenium in the accompanying paper. The interacting groups have C_{2v} symmetry and the C_2 operation is the only one in common with the crystal operations. There are three B_1 and three B_2 coordinates all of which are antisymmetric under the C_2 operation. However, interactions between the B_1 and B_2 coordinates are not considered in the force constant fitting.

The secular equation is obtained without the necessity of removing redundant coordinates because the kinetic energy is expressed in terms of coordinates (linearly independent) which are convenient for the kinetic energy, and not vice versa as in the FG method. In addition, none of the coordinates for the kinetic energy involves displacements of atoms outside of one primitive cell. Therefore, the kinetic energy matrix does not depend on κ. These are very practical properties for simplifying calculations.

The basis vectors in Eq. (6.4) (or the vectors derived from them which belong to the group of the wave vector) are useful for finding a secular equation which gives approximate normal modes and frequencies for those modes in molecular crystals which can be described in terms of translations and rotations of the molecules. This is done by using only the basis vectors $\hat{\mathrm{L}}_{\bar{x}}, \ldots, \hat{\mathrm{L}}_{r\bar{z}}$ as defined in Eqs. (6.2) and (6.3) for each molecule in forming the $\hat{\mathrm{L}}_{\mathrm{cell}}$ matrix in Eq. (6.4). This procedure will work regardless of how the intermolecular potentials are expressed.

It should be noted that the relative motion coordinates are given in terms of axes within the groups with origins determined by Eq. (3.1), and for origins of interacting groups constrained by Eq. (3.19). These origins may not be at the centers of mass of the groups, or of the interacting set. The relative motion coordinates are essentially different in this respect from the coordinates used to express the kinetic energy as defined in Eqs. (6.2)–(6.4).

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[1]The applications considered here assume that the coordinates can be expressed adequately to only linear terms in the Cartesian displacements. This is rigorous if there is no redundancy among the coordinates. If redundancy is present the quadratic dependences of the redundant coordinates can introduce extra terms into the potential; see M. C. Pomposiello, H. Bonadeo, and E. D'Alessio [Chem. Phys. Lett. **35**, 379 (1975)] for a comparison of results with and without neglect of the extra terms.

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